



Influence of H₂SO₄ and ferric iron on Cd bioleaching from spent Ni–Cd batteries

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ABSTRACT

The paper is concerned with biohydrometallurgical methods of cadmium recovery from spent Ni–Cd batteries. Cd leaching efficiency from electrode material in different media (H₂SO₄ and Fe₂(SO₄)₃ solutions), at different Fe(III) concentrations and using the bacteria *Acidithiobacillus ferrooxidans* were investigated. The main aim of this study was to understand which from the bioleaching products (sulphuric acid or ferric sulphate) play a main role in the bioleaching process of Cd recovery. The influence of Fe ions on Cd leachability was confirmed. The best leaching efficiency of Cd (100%) was reached by bioleaching and also by leaching in Fe₂(SO₄)₃ solution. The results of X-ray diffraction confirmed that no cadmium was present in solid residuum obtained after the Cd bioleaching as well as Cd leaching using solely ferric iron. The use of H₂SO₄ solution resulted in the lowest efficiency of Cd leachability, the presence of hydroxides in electrode materials caused neutralization of the leaching solution and inhibition of Cd leaching.

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1. Introduction

Spent Ni–Cd batteries contain a high amount of heavy metals (51–67%) therefore the interest associated with valuable metal recovery has become more increasing. Electrode material contains up 22–46% of Cd (Vassura et al., 2009) depending on the type of Ni–Cd batteries while in the Earth's crust cadmium makes up about 0.1–0.5 ppm. In nature cadmium occurs as a part of other minerals (e.g. Cd content in sfalerite is 0.6%, in galena 0.02%, in chalcopyrite 0.12%). Cadmium has many common industrial uses as cadmium pigments (11%), stabilizers and alloys (3%), coatings (7%) and it plays a key role in battery production (79%) (ICdA, 2012). In the past a little amount of Cd (~10%) was obtained by recycling process, especially, by recycling of ash from steel processes.

EU Member States have committed themselves to adhere to the EU Battery Directive which ordered 25% collection target by September 2012. EBRA (European Battery Recycling Association) ensures the recycling of more than 85% of the spent batteries of the EU market. Based on EBRAs statistics for the year 2010 was find 18% increase in recycling Ni–Cd spent batteries compared to 2009 (EBRA, 2010). However, the actual number of recycled batteries is higher because it is necessary to take into account the processors who are non members of EBRA (CITRON, 2012).

In comparison with Cd mining, recovery of cadmium by the recycling process is environmental friendly and economically more convenient. Several processes of spent Ni–Cd batteries treatment based on pyrometallurgical (Sumitomo, Snam-Savam, Sab Nife, Waelz, Accure processes, vacuum metallurgy separation), hydrometallurgical (TNO, BATENUS processes) and combined processes (Recytec proces) have been developed so far (Espinosa et al., 2004; Nogueira and Margarido, 2004; Rudnik and Nikiel, 2007; Karnchanawong and Limpiteeprakan, 2009; Huang et al., 2010). Due to the great energy consumption, high cost, low efficiency and serious secondary pollution the conventional techniques generally used for metal recovery from low grade ores and waste has been gradually replacing by the alternative and more efficient technology, which is biohydrometallurgy. Biohydrometallurgical processing of solid waste is similar to natural biogeochemical metal cycles and reduces the demand of natural resources, energy and landfill space (Brierley and Brierley, 2001; Zhu et al., 2003; Bernardes et al., 2004; Nogueira and Margarido, 2007; Ndlovu, 2008; Brierley, 2008). This technology can be also successfully applied for recycling of such waste as batteries or electronic scrap consisted of heterogeneous material like ceramics, polymers and also higher amount of different metals compared with natural sources.

A key microorganism in metal bioleaching from sulfide ores is the iron and sulphur oxidizing bacterium *Acidithiobacillus ferrooxidans*, which has been studied extensively. Different from metals sulfides the spent Ni–Cd batteries are characterized by elemental metals, metal oxides and hydroxides therefore different bioleaching mechanisms of this non-sulphidic waste may be expected

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(Vassura et al., 2009; Huang et al., 2011). It is of value to find the main factors responsible for metal recovery by bioleaching since each material obtained is to a certain extent specific and requires distinctive treatment.

The main aim of our work was to examine the influence of leaching agents (sulphuric acid and ferric sulphate) on the bioleaching of particular metal in detail. Therefore chemical leaching using two different media was carried out in order to simulate the effect of particular metabolites microbially produced during bioleaching process on cadmium recovery from spent Ni–Cd batteries. The first one was based on the leaching ability of sulphuric acid and the second one on the leaching ability of ferric iron at the same and different concentration (18 g/l, 9 g/l, 4.5 g/l and 0.9 g/l Fe) as that of present in 9 K medium (9 g/l Fe).

2. Experimental materials and methods

2.1. Characteristics of used Ni–Cd batteries

In this research spent rechargeable Ni–Cd battery pack, model NO OF31NC 5H for cordless drill was used as an experimental material. Batteries were weighted and manually cut up into different portions. The mean weight of batteries was 40 g. Electrode material forms about 55% of the battery weight (cathode 11 g and anode 12 g). All remaining components of battery were metal parts (16 g) and separator with plastic parts (3 g).

For experiments cathode and anode electrode materials were used separately. To obtain the electrodes, the steel case was manually opened and rolled electrodes were separated. The active electrode material, cathode and anode powders were physically removed from the metal grid, ground and sieved to obtain a mesh size of less than 40 µm.

AAS analysis results of the cathode and anode input samples showed that the content of cadmium in the battery was 6.5% and 38% for the cathode and anode respectively. X-ray diffraction showed that the anode was covered by cadmium and cadmium hydroxide in combination with metallic Ni while the cathode was covered by nickel hydroxide and nickel oxy-hydroxide. Cathode also contains additives and conducting agents (graphite or Ni powder) and a small amount of cadmium. A small amount of cobalt was also present in both samples (Figs. 1 and 2).

2.2. Experimental set-up

2.2.1. Bacteria

A pure culture of *A. ferrooxidans* was obtained from the Institute of Geotechnics of Slovak Academy of Science, Košice. The organism was cultured in Erlenmeyer flasks containing 200 ml of 9 K

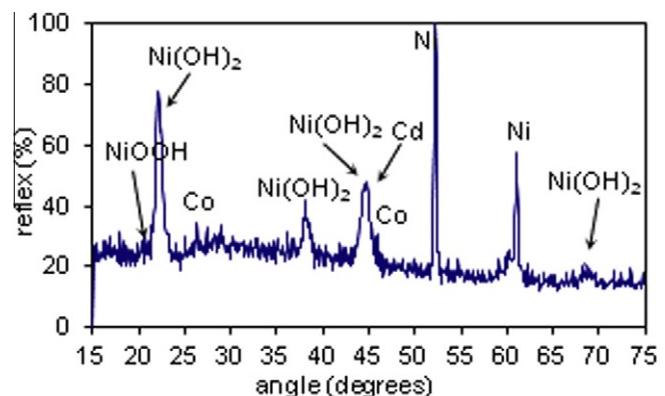


Fig. 2. X-ray diffraction pattern of the initial cathode material of spent Ni–Cd battery.

medium (Silverman and Lundgren, 1959) at initial pH 1.5 at 30 °C. The basic 9 K medium was composed of $(\text{NH}_4)_2\text{SO}_4$ – 2.0 g, KH_2PO_4 – 0.25 g, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ – 0.25 g, KCl – 0.1 g, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ – 44.2 g and distilled water, 1000 ml. The same medium was also used for the bioleaching experiments.

2.2.2. Leaching experiments

Experiments were carried out separately with the cathodic and anodic material obtained from nickel–cadmium batteries in three different media:

1. Bioleaching media (9 K medium).
2. H_2SO_4 solution.
3. $\text{Fe}_2(\text{SO}_4)_3$ solution.

In order to follow the importance of sulphuric acid and ferric iron the chemical leaching was conducted in media with H_2SO_4 and $\text{Fe}_2(\text{SO}_4)_3$ without bacteria. The H_2SO_4 solution was prepared by dilution of 96% H_2SO_4 in distilled water to obtain the final pH value of 1.5 (0.15% H_2SO_4 solution). The leaching medium with $\text{Fe}_2(\text{SO}_4)_3$ was prepared using the different concentration of ferric irons, 18 g/l, 9 g/l, 4.5 g/l and 0.9 g/l. The final pH values were adjusted to 1.5 with 5 M NaOH. To the prepared media 2 g of the cathodic and anodic powder material, respectively, was added. Simultaneously 2 g of electrode powder was added to the 200 ml of 9 K medium with cultured bacteria and incubated at 30 °C. After 3 weeks, when the medium colour turned into redbrown due to the $\text{Fe}(\text{III})$ formation, 5 ml of adapted bacteria were poured into the Erlenmeyer flask containing 295 ml of pure 9 K medium. After 4 days of precultivation 3 g of electrode material was added.

The experiments were carried out in the incubator at 30 °C, the solid/liquid (w/v) ratio was 1/100 in all flasks. The initial pH values of all three media were adjusted to 1.5. The samples for analysis were withdrawn at these days: 1, 3, 7, 10, 13, 21, and 28. All experiments were conducted in triplicates.

2.2.3. Analytical determinations

The pH of each experiment was measured throughout the experimental period by pH meter GRYF 208 L using a combine electrode.

The leachant (5 ml) was periodically taken and filtrated. Cd concentration in each filtrate was determined by Atomic Absorption Spectrometry (AAS) (SpectraAA 20 PLUS VARIAN at 326 nm).

Chemical composition of the initial cathodic and anodic material and the final leaching residues was determined by AAS and X-ray diffraction (URD-6 (Rich. Seifert-FPM, German), radiation source Co).

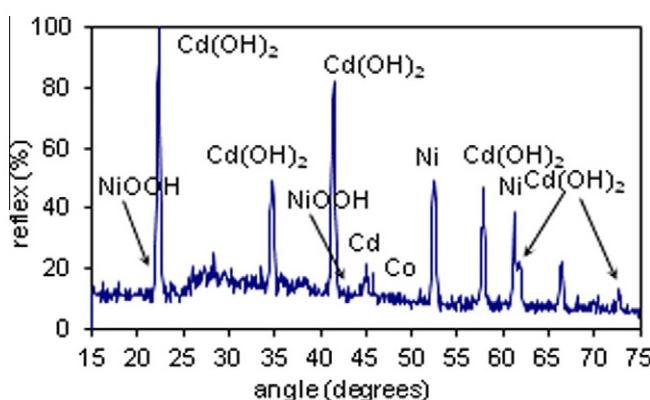


Fig. 1. X-ray diffraction pattern of the initial anode material of spent Ni–Cd battery.

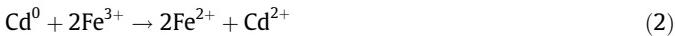
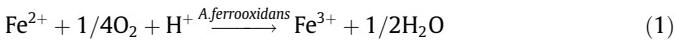
3. Results and discussion

3.1. Efficiency of Cd recovery by bioleaching

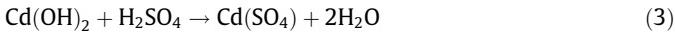
The overall Cd bioleaching efficiency was 100% and 98% for cathodic and anodic material, respectively.

As it can be seen in Fig. 3 the beginning of the leaching curves of both electrode material starts at about 40% of yield in the first day of bioleaching which corresponds to the dissolution of cadmium hydroxides in the first hours of the leaching process. The bioleaching rate is the highest during the first 7 days and during that time majority of Cd is dissolved from anodic material and on the following days the process rate is slowing down. However, in the case of cathodic material Cd bioleaching is gradually increasing until the 28th day. As there is the different chemical composition of both electrode materials and the anodic material mainly consists of cadmium hydroxides being much more soluble than metallic cadmium, the attack of anodic material is faster than corresponding to cathodic material. It is also necessary to take into account the toxicity of a higher amount of Cd on bacteria resulting in the inhibition of bioleaching process.

Fe(II) ions acted as a source of energy for bacterial growth during the bioleaching process, oxidized into Fe(III) ions that as strong oxidation agents caused the solubilization of Cd (1), (2).



Based on the fact that pH value of the solution increased slightly throughout the bioleaching process, maximal pH value was measured 2.8 (Fig. 4), it can be assumed that there was a balance between the simultaneous consumption of protons during the oxidation of Fe(II) ions as well as cadmium hydroxides neutralisation (3) and release of protons during the hydrolysis of Fe(III) ions (4, 5, 6):



Simultaneously, jarosite precipitation occurred (7) that caused that the equilibrium of Fe(III) ion hydrolysis was shifted towards the right and thus other proton ions were released into the

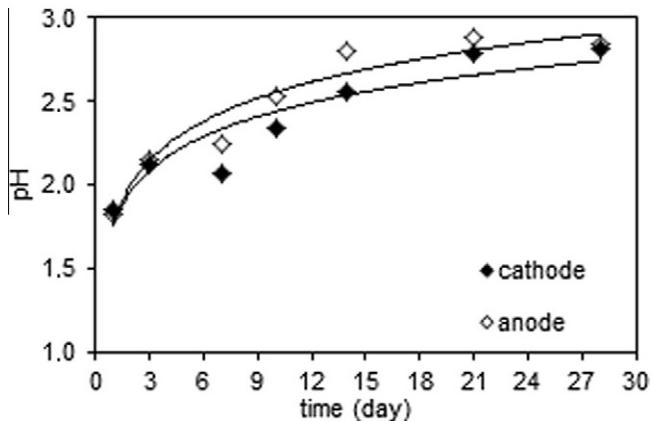
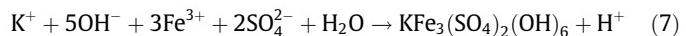


Fig. 4. Dependence of pH on time of leaching.

solution. Jarosite presence was confirmed by X-ray diffraction. Jarosite formation has generally negative effect in the metal leaching process because of its adsorption ability and creation of kinetic barriers due to the small diffusion of reactants and products through the precipitation zone (Jensen and Webb, 1995). It can explain the inhibition of bioleaching process and subsequently the slower dissolution of Cd in the case of the cathodic powder bioleaching.



Based on the results of X-ray diffraction (Fig. 5) of anodic powder residuum after bioleaching process it can be also seen in addition to jarosite mass, the presence of negligible amount of cadmium hydroxides and metallic nickel. X-ray diffraction of the cathodic residuum confirmed the presence of a small amount of metallic nickel and jarosite and also the complete dissolution of metallic cadmium (Fig. 6).

Based on the published results sulfuric acid and ferric iron are considered to be the main factors responsible for bioleaching of metal sulfides. Since the bioleaching mechanism of non-sulfide ores and waste has not been explained sufficiently the question raised which of the two factors appeared to be the major factor responsible for the Cd release from Ni-Cd batteries. The effect of each factor (acidity and presence of Fe(III) ions) was examined separately in following experiments.

3.2. Efficiency of Cd leaching in H_2SO_4 solution

The results of chemical leaching in the presence of H_2SO_4 at initial pH value of 1.5 are shown in Fig. 7. The overall Cd leaching

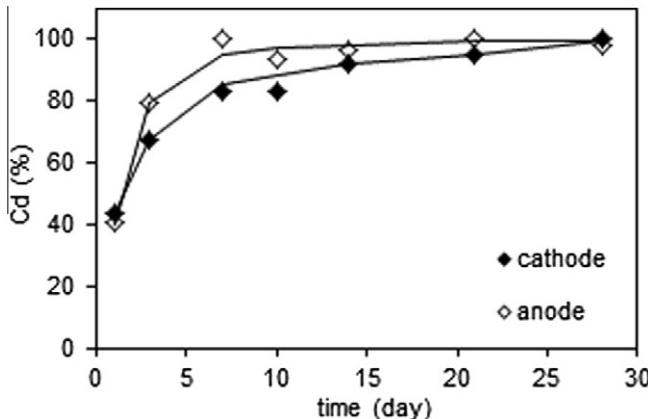


Fig. 3. Cd leaching yields in 9 K solution with *Acidithiobacillus ferrooxidans* bacteria.

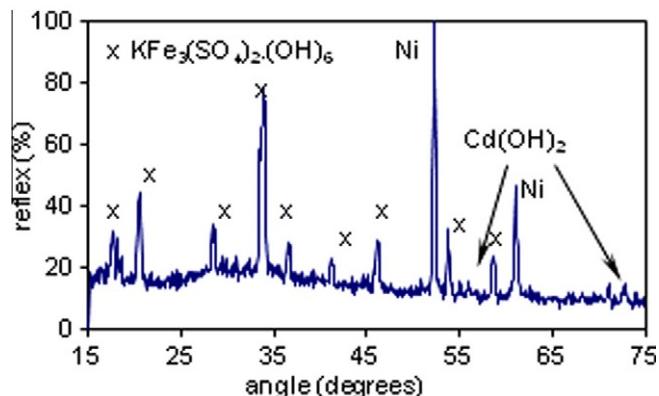


Fig. 5. X-ray diffraction pattern of bioleached anode material.

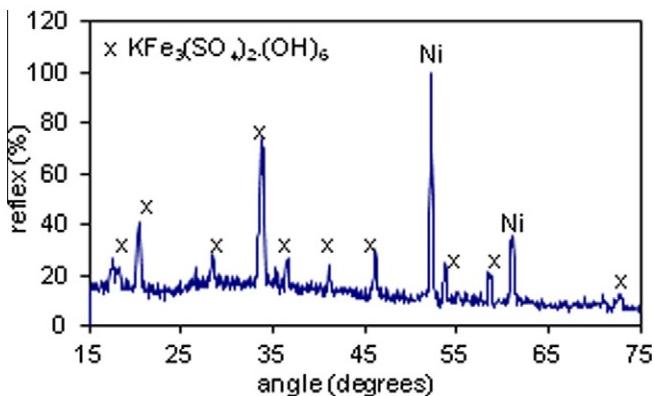


Fig. 6. X-ray diffraction pattern of bioleached cathode material.

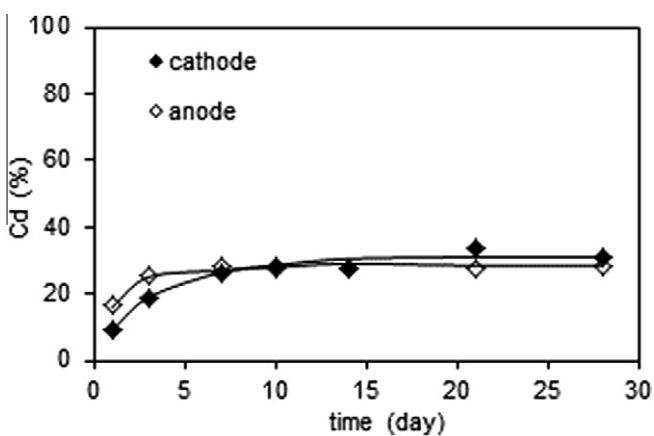


Fig. 7. Cd leaching yields in solution by leaching of cathode and anode powder in H₂SO₄ solution.

efficiency was ~30% and ~28% for cathodic and anodic powder material, respectively.

According to the curve of cathode leaching it is apparent that the amount of Cd dissolved into the solution increased up to the 7th day of the leaching process. The increase of Cd leaching was coincident with consumption of sulphuric acid leading to the inhibition of Cd dissolution (Fig. 8).

Chemical leaching of Cd in H₂SO₄ solution under our conditions involves neutralization reaction (3) needed for dissolution of Cd

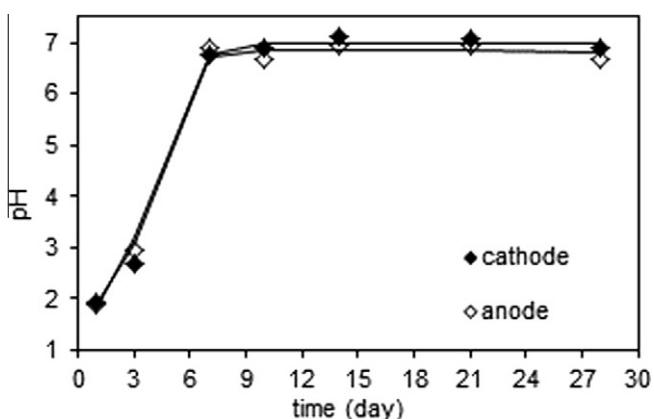


Fig. 8. Dependence of pH on leaching time.

and without other factors added such as abundance of acid or presence of Fe(III) ions further Cd dissolution will not occur.

The chemical composition of final leaching residuum was determined by X-ray diffraction (Fig. 9). The results of cathodic material analysis confirmed the complete dissolution of cadmium hydroxides and presence of metallic Cd and CdO. In the case of final anodic material the higher amount of cadmium hydroxides remained in the residuum (Fig. 10) that can be associated with the chemical composition of both electrode materials.

From the chemical point of view, higher Cd leaching efficiency could be reached by the addition of sulfuric acid into the medium with the absence of the bacterium, however, the process itself would have become economically less effective.

3.3. Efficiency of Cd leaching in Fe₂(SO₄)₃ solution

The results of chemical Cd leaching from both electrode materials using different concentrations of Fe(III) ions are shown in Fig. 11. The chemical leaching using the same ferric iron concentration as that in 9 K medium was slower compared with the bioleaching experiment, when the maximum Cd release (100%) from anodic materials was reached on the 14th day, while, in the case of the Cd bioleaching it was much earlier, on the 7th day. In the first 7 days of the bioleaching of cathodic materials the process rate had been increasing and later gradually slowing down until the 28th day when the whole Cd was released. However, during the chemical leaching using Fe(III) ions without any bacteria the leaching process rate had been gradually increasing in the first 14th days, when 90% Cd release was reached. After that the leaching process rate decreased and the whole cadmium was completely leached on 28th day. The pH values throughout the leaching experiment increased just a little, from the initial pH of 1.5 up to 2.3 (Fig. 12). To maintain the low pH values was possible due to the ferric sulphate hydrolysis that caused the release of protons into the solution and jarosite formation owing to precipitation of ferric hydroxides and parts of the sulphate (as presented in the Section 3.1). The results obtained showed that ferric iron played more important role in the Cd leaching than sulfuric acid therefore the question raised to what an extent ferric iron could influence Cd release into the solution. Subsequently the influence of different Fe(III) concentration on the Cd leaching was further examined (Fig. 11).

The results of Cd leaching of both electrode materials during Cd leaching process in the presence of a double amount of Fe(III) ions (18 g/l) as that present in 9 K medium were very similar to those described above, although, in the case of anodic material the leaching process rate in the first days of Cd leaching was slightly higher (Fig. 11). Cd extraction during the leaching of cathodic material in

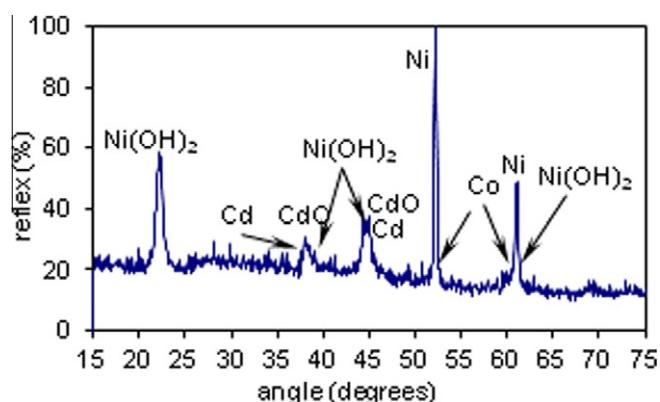


Fig. 9. X-ray diffraction pattern of the cathode leached in H₂SO₄ solution.

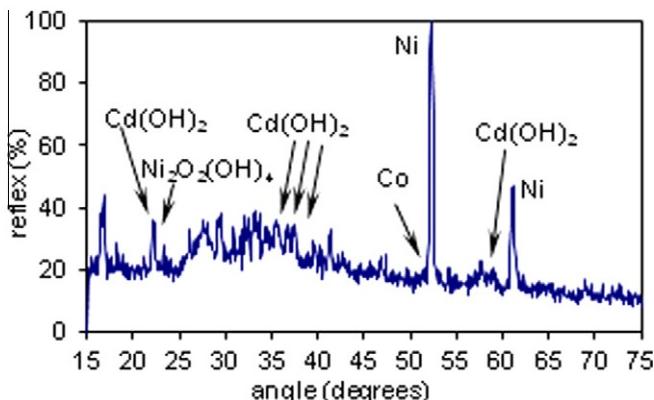


Fig. 10. X-ray diffraction pattern of the anode leached in H_2SO_4 solution.

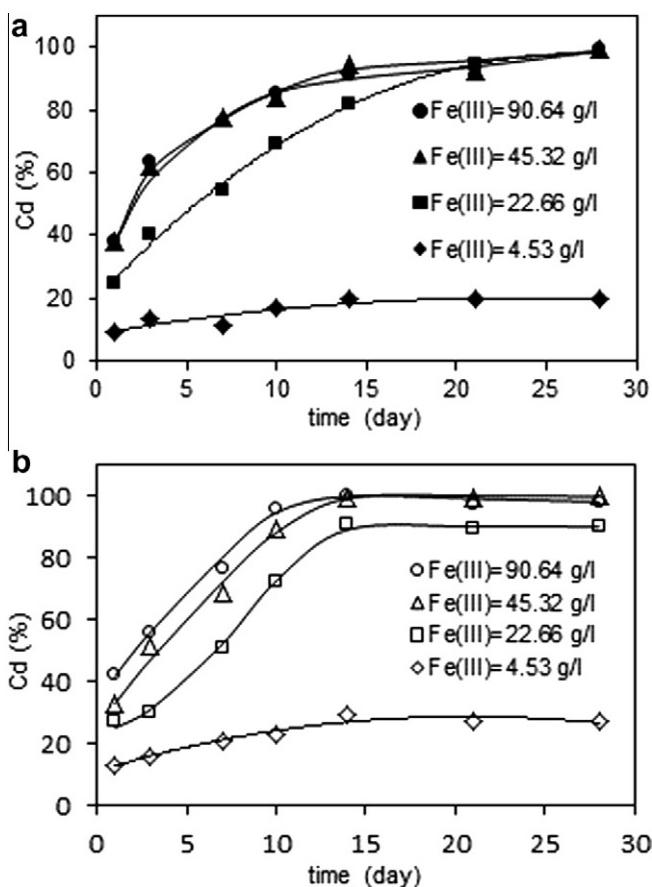


Fig. 11. Cd leaching yields by leaching of cathode (a) and anode (b) powder in the solutions with different Fe concentrations.

the presence of Fe(III) concentration (4.5 g/l) corresponding to 50% of total iron concentration in 9 K medium was slower, however, the highest Cd leaching efficiency, 100%, was also reached on the 28th day. Cd leaching curves of cathodic material using the lowest Fe(III) concentration (0.9 g/l) corresponding to 10% of total iron concentration in 9 K medium focused on the slowest and less effective leaching process of Cd. In the case of Cd leaching of anodic material the lower Fe(III) concentrations (4.5 g/l, 0.9 g/l) resulted in slowdown of leaching process rate and a low Cd dissolution. The different Cd dissolution may be associated with the chemical composition of both electrode materials. Based on the results it

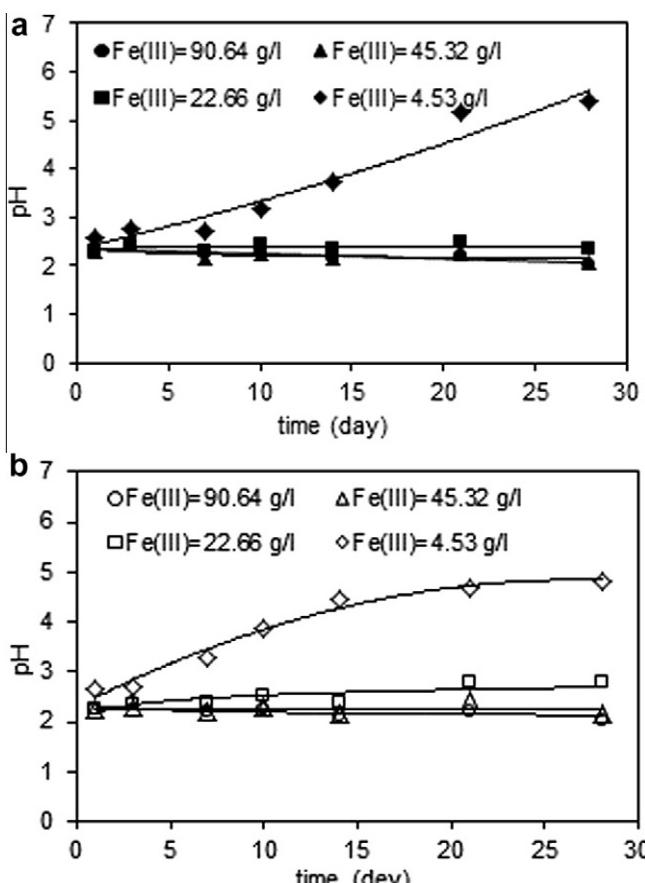


Fig. 12. Dependence of pH on leaching time: (a) cathode, (b) anode in the solutions with different Fe concentrations.

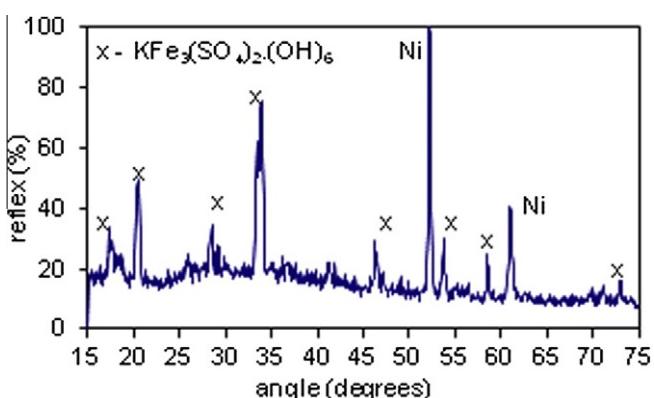


Fig. 13. X-ray diffraction pattern of the anode material leached in ferric iron solution.

seems that amount of iron used for chemical leaching of Cd from Ni–Cd spent batteries contributes to maintain more or less constant pH values and to a great extent influences Cd extraction.

The presence of jarosite mass and no presence of Cd in the final residuum of both electrode materials were confirmed by X-ray diffraction (Figs. 13 and 14). Decreased production of jarosite is assumed to be due to the gradual transformation of ferrous into ferric iron during the bioleaching in comparison with chemical leaching process. Further investigation is needed to find out why the bioleaching process rate is faster.

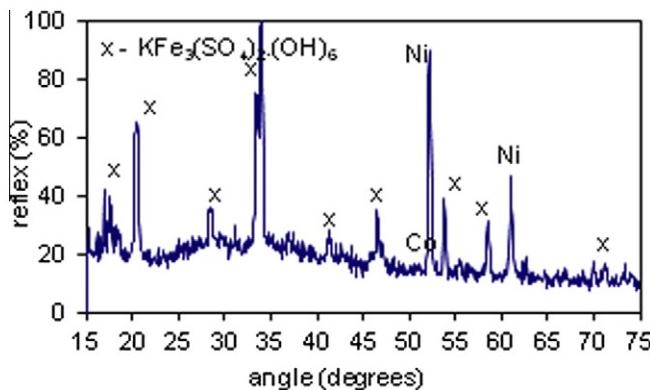


Fig. 14. X-ray diffraction pattern of the cathode material leached in ferric iron solution.

4. Conclusions

Chemical simulation of bioleaching process of Cd dissolution from Ni–Cd batteries in the media with sulphuric acid and ferric iron, respectively, was carried out to evaluate the influence and effect of particular factors involved the Cd bioleaching from spent Ni–Cd batteries. Research revealed:

- The bioleaching using the bacterium *A. ferrooxidans* is the effective way of cadmium recovery from non-sulfidic waste as Ni–Cd batteries. Ferric iron as one of the main leaching agents plays the important role not only as the strong oxidative agents but also as a factor that can maintain the low pH throughout the experimental period, the environment needed for the Cd release, due to its hydrolysis. Cd bioleaching process rate was higher in comparison with the chemical leaching with solely ferric iron at the same concentration as that in 9 K medium (9 g/l) since almost 100% Cd was released in the first 7th days.
- In the case of chemical simulation of Cd dissolution in the acid media at the same conditions as that in bioleaching but without bacteria the pH increased rapidly due to the acid consumption resulting in the inhibition of Cd leaching. In order to keep constant low pH the addition of sulphuric acid would be needed; however, from economical point of view this is less effective.

Acknowledgement

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